



# Synthesis of high-activity $\text{TiO}_2$ photocatalyst via environmentally friendly and novel microwave assisted hydrothermal process

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## ABSTRACT

This work focused on the synthesis of high-activity titania photocatalysts through an environmentally friendly and novel process. A high energy-efficient microwave-assisted hydrothermal method was employed to prepare  $\text{TiO}_2$  from commercially available  $\text{K}_2\text{Ti}_4\text{O}_9$  particles without using any organic species. The obtained titania consisted of small particles around 5 nm in diameter and high specific surface areas above  $200 \text{ m}^2/\text{g}$ . The photocatalytic activities were evaluated by the photo-decomposition of acetaldehyde. The titania prepared through this process showed high photocatalytic activities equal to the commercial one, AEROXIDE<sup>®</sup>  $\text{TiO}_2$  P 25.

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## 1. Introduction

A variety of environmental problems now affect our world, among which air pollution is one of the largest problems. A person inhales on average about 20,000 L of air a day. Every time we breathe, we risk inhaling dangerous chemicals in the air. Therefore, the purification of polluted air is an urgent problem. The use of photocatalysts in environmental pollution control is a clean process, since it is driven by the clean energy of sunlight.

Photocatalysis has recently become a common word and various products using photocatalysis have been commercialized. Although many kinds of compounds have been found to show photocatalytic activities, only  $\text{TiO}_2$  has been used commercially, until now, due to its excellent photocatalytic activity and chemical stability [1].

Since the discovery of photocatalytic splitting of water on a  $\text{TiO}_2$  electrode in 1972 [2], great efforts have been made to promote the activity of  $\text{TiO}_2$ . Besides the activity, the cost of photocatalyst is a crucial parameter. In addition, attention should also be paid to the formation of photocatalyst to relieve possible environmental pollution during the synthesis of photocatalyst.

Based on the above concept, synthesis of high-activity  $\text{TiO}_2$  photocatalyst through an environmentally friendly and novel microwave assisted hydrothermal process from a commercially

available raw material was attempted in this study. The microwave assisted hydrothermal method shows a rapid heating rate, molecular homogeneity and selective heating of reaction solutions in comparison with the conventional hydrothermal method. As a result, the reaction time could be reduced by several orders of magnitude, and consequentially, higher energy efficiency could be achieved [3–5].

Common Ti sources used in hydrothermal synthesis usually include titanium tetrachloride [6,7], titanium isopropoxide [8,9], titanium butoxide [10,11], etc. Due to the high moisture activity,  $\text{TiCl}_4$  hydrolyzes easily in the air which makes handling it difficult.  $\text{Ti}(\text{OPr})_4$  and  $\text{Ti}(\text{OBu})_4$  are much more stable, but organic solvents are usually used during the synthesis [8–11] which would make it difficult for industry to utilize the process, due to the necessity of waste water treatment. In contrast, in this study,  $\text{K}_2\text{Ti}_4\text{O}_9$  was applied as a raw material. It has been widely used as an ion exchanger [12], friction material [13], etc. In comparison with above Ti sources, it is more stable, safe and easier to handling.

## 2. Experimental

### 2.1. Synthesis

Commercial  $\text{K}_2\text{Ti}_4\text{O}_9$  (Otsuka Chemical Co. Ltd., Tokyo, Japan) was first washed in hot water to eliminate impurities. Then, 4 g of the powder was put into a zirconia pot with an internal volume of  $45 \text{ cm}^3$  with seven zirconia balls, each 15 mm in diameter, and dry milled for 2 h using a planetary ball mill (Pulverisette-7, Fritsch,

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Germany) at 700 rpm rotation speed under room temperature. The obtained fine powders were allowed to react with a 5 M HCl aqueous solution at 60 °C under vigorous stirring to obtain a colloidal solution. After reacting for 5 h, the solution was filtered in order to eliminate the remaining large powder. The liquid in the filter consisted of a clear transparent colloid and was collected and used as a Ti precursor solution. Next, concentrated NH<sub>3</sub> aqueous solution was added in drops into the Ti precursor solution to adjust the solution pH to zero. Following, the solution was transferred into a Teflon tube, sealed and heated by microwave irradiation at 190 °C for a desired length of time. In comparison, the reaction was also carried out by heating in an electric oven at 190 °C for 90 min. The generated precipitate was separated by centrifugation, followed by rinsing with distilled water and ethanol. Finally, the obtained product was dried in a vacuum at 60 °C overnight.

## 2.2. Analysis

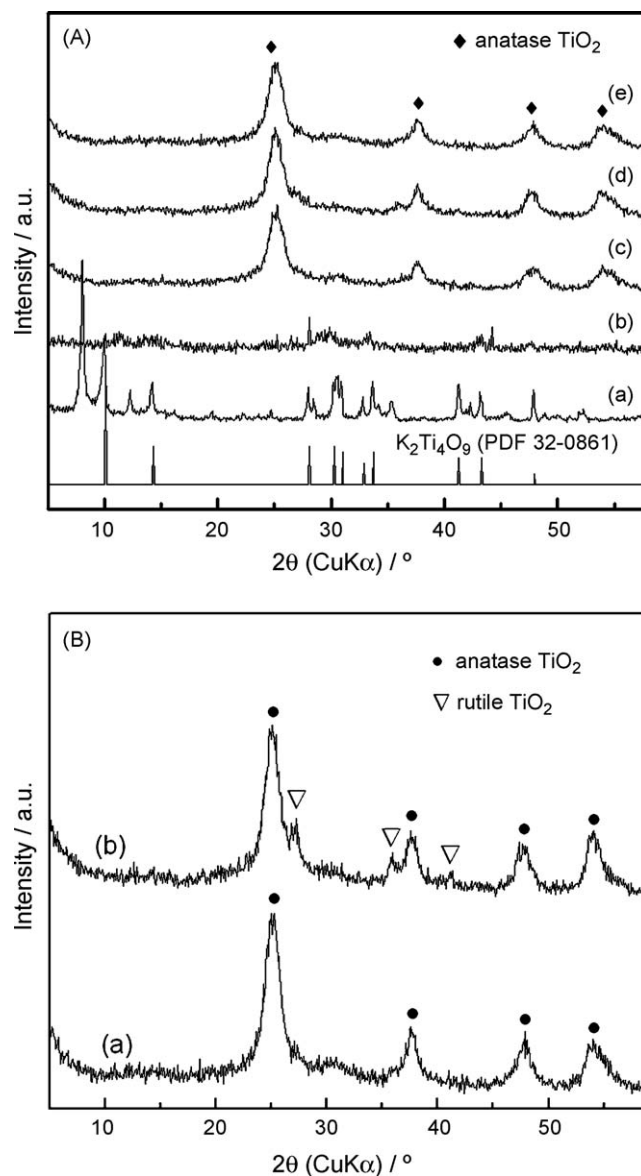
The crystalline phase of the product was identified by X-ray diffraction analysis (XRD, Shimadzu XD-D1) using graphite-monochromized Cu K $\alpha$  radiation. The specific surface area of the sample was measured by a surface area and pore size analyzer (Quantachrome Instruments, NOVA 4200e). The morphology and particle size were observed through a transmission electron microscope (TEM, JEOL, JEM-2010). A Fourier transform infrared spectroscopy (Varian, 7000 FT-IR) was employed to investigate the surface conditions of the sample.

## 2.3. Photocatalytic reactions

The photocatalytic activity for acetaldehyde degradations was evaluated by measuring the changes in the concentrations of acetaldehyde and the decomposition product CO<sub>2</sub>. In order to obtain a homogeneous sample film for photocatalytic characterization, 0.4 g of sample powder was sufficiently mixed with 0.96 g xylene and 0.96 g 2-butanol, then dispersed on a glass substrate with an area of 6.4 cm  $\times$  12 cm (76.8 cm<sup>2</sup>). The sample film was then heated at 140 °C for 30 min to evaporate the organic solvents. After irradiation using a 10 W black light for 1 h to eliminate the adsorbed organics on the surface, the sample film was placed in a sealed opaque reaction vessel (28 L), together with 40  $\mu$ L of liquid acetaldehyde (99%, Kanto Chem.). The acetaldehyde was rapidly turned into a gas by heating with an electric heater and an electric fan, which were set in the inside of the reaction vessel. The catalyst was kept in the dark for at least 40 min to realize the adsorption-desorption equilibrium, then, 352 nm of UV light (black light) was irradiated to start the photocatalytic reaction. The average light intensity irradiated on the catalyst surface was about 6.0 mW cm<sup>-2</sup>. About 5.0 mL of gas was withdrawn from the reaction vessel through the injection hole every 30 min to determine the concentrations of the remaining acetaldehyde and generated CO<sub>2</sub> using a gas chromatograph (GC-2014 SHIMADZU).

## 3. Results and discussion

Fig. 1(A) illustrates the XRD patterns of the raw material of commercial K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> and the samples prepared under various reaction conditions by microwave-assisted hydrothermal treatments. Most of the diffraction peaks observed on the raw material (a) could be assigned to K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> (PDF 32-0861). Several extra peaks around 8° and 12° might be attributed to the diffractions of K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>·2.2H<sub>2</sub>O (PDF 39-0043). The planetary ball-milling treatment caused drastic weakening and broadening of the diffraction peaks, as observed in sample (b), which was attributed to the decrease in particle size together with the destruction of the



**Fig. 1.** (A) XRD patterns of (a) K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>, (b) ball-milled K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>, and TiO<sub>2</sub> prepared at 190 °C for (c) 10 min, (d) 30 min, and (e) 90 min by the microwave assisted hydrothermal method. (B) XRD patterns of TiO<sub>2</sub> prepared at 190 °C for 90 min by (a) the microwave assisted and (b) conventional hydrothermal method.

crystalline structure. Parallel experimentation revealed that this step was quite important for preparing TiO<sub>2</sub> from K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>. If K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> directly reacted with HCl without ball-milling, instead of the transparent Ti precursor solution, protonated tetratitanate, H<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>, would be obtained [14].

After the microwave reaction, regardless of the reaction time, all the obtained products showed single anatase phase of TiO<sub>2</sub>. The formation mechanism might be considered as “low temperature dissolution-precipitation process” [15]. It is worthy to mention that it is possible to obtain crystallized TiO<sub>2</sub> particles even when the reaction time is as short as 10 min, although it usually took more than 2 h by the conventional hydrothermal method [15,16]. These differences may be due to the high efficiency of microwave heating, indicating that the reaction time together with the energy consumption was drastically reduced by microwave heating.

The prepared TiO<sub>2</sub> showed broad diffraction peaks. Using Scherrer's Equation, the crystallite sizes were calculated to be around 5 nm. This value agreed well with that observed from TEM analysis.

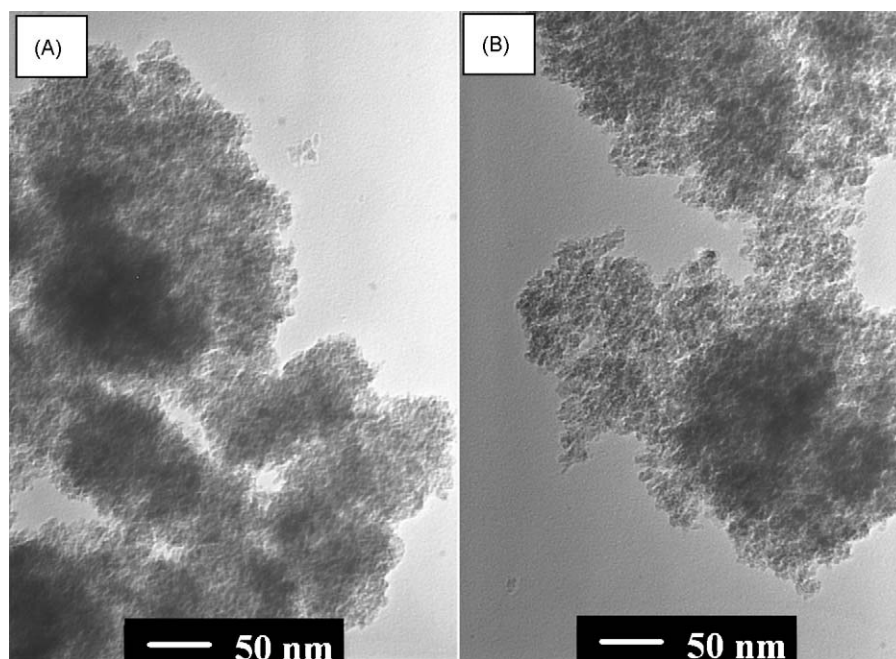


Fig. 2. TEM images of the  $\text{TiO}_2$  powders prepared at  $190^\circ\text{C}$  for (a) 10 min and (b) 90 min.

Fig. 1(B) shows the XRD pattern of the sample obtained from conventional hydrothermal reaction. It showed a mixed phase consisting of anatase and rutile. Comparing with the microwave-assisted hydrothermal treatment, it took a longer time to heat up the solution to the desired temperature. Therefore, the phase transformation of the anatase proceeded the more stable rutile phase during heating.

Fig. 2 shows the TEM images of the  $\text{TiO}_2$  prepared under different reaction conditions. It was found that the reaction time did not obviously influence the morphologies of the products. All the prepared samples showed similarly small crystallite sizes of around 5 nm in diameter, and slight agglomeration was also observed. The small crystallite sizes of the prepared  $\text{TiO}_2$  were considered due to the high efficiency of microwave heating. Under microwave irradiation, the temperature of the reaction solution is raised so rapidly that a large amount of nuclei can be generated in a very short time, which inhibited the crystal growth of the product.

As a result of the small crystallite size, the prepared  $\text{TiO}_2$  showed quite high specific surface areas above  $200\text{ m}^2/\text{g}$  as shown in Table 1. The specific surface area did not change that much when changing the reaction time from 10 to 90 min. The  $\text{TiO}_2$  prepared by the conventional hydrothermal method also showed a high specific surface area of  $218\text{ m}^2/\text{g}$ .

Fig. 3(A) shows the Fourier transform infrared spectra of the  $\text{TiO}_2$  samples prepared by the microwave assisted hydrothermal reactions at  $190^\circ\text{C}$  for (a) 10 and (b) 90 min, and (c) after calcination of sample (b) at  $400^\circ\text{C}$ . Comparing the FT-IR spectra of samples (a) and (b), it is observed that bands at a low wave number range corresponding to the Ti–O and Ti–O–Ti groups [17] did not change with the reaction time. In contrast, the band at  $1440\text{ cm}^{-1}$  which is assigned to the asymmetric bending vibrations of  $\text{NH}_4^+$  greatly decreased with time [18,19]. This result suggested that prolonged reaction time could decrease the amount of ammonium ion adsorbed on the surface of  $\text{TiO}_2$ . Comparing the FT-IR spectra of

samples (b) and (c), it is obvious that after calcination at  $400^\circ\text{C}$ , the broad band between  $3600$  and  $2800\text{ cm}^{-1}$ , assigned to the stretching vibrations of hydroxyl groups and ammonium species, greatly decreased. The sharp band at  $1630\text{ cm}^{-1}$  was weakened drastically and diverged into two peaks which could be assigned to the bending related to molecular water and symmetric bending vibrations of  $\text{NH}_4^+$ , respectively. The asymmetric bending vibrations of  $\text{NH}_4^+$  at  $1440\text{ cm}^{-1}$  also became weaker. These results suggest that the longer hydrothermal reaction time or post-hydrothermal reaction calcination promoted the crystallization of  $\text{TiO}_2$  by decreasing the amounts of  $\text{OH}^-$  group and  $\text{NH}_4^+$  absorbed on the surface.

Fig. 3(B) shows the FT-IR spectra of the  $\text{TiO}_2$  obtained by the conventional hydrothermal reaction at  $190^\circ\text{C}$  for 90 min. The sample showed almost the same spectrum as that prepared by microwave assisted hydrothermal reaction, indicating a sharp band at  $1630\text{ cm}^{-1}$ , corresponding to the bending of molecular water and  $\text{NH}_4^+$  specie. The difference in crystalline phase of the sample could not be observed on FT-IR spectra.

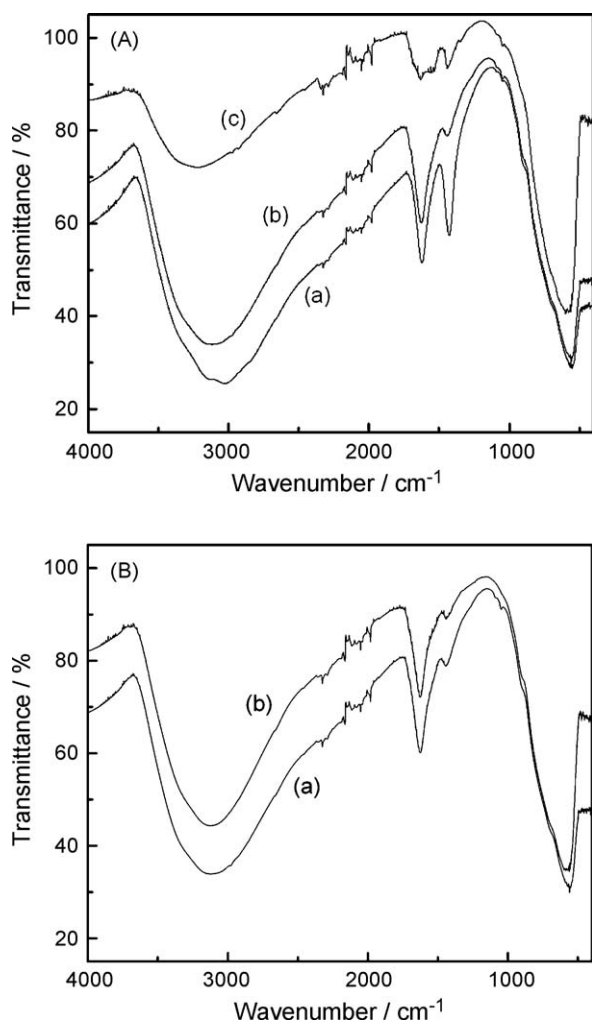
The influence of the microwave-assisted hydrothermal reaction time on the activities in the photodecomposition of acetaldehyde is shown in Fig. 4(A). The blank experiment without sample powder showed that acetaldehyde is very stable, and it could not be decomposed under UV light irradiation without photocatalyst. It is obvious that both the decomposing rate of acetaldehyde and the generating rate of carbon dioxide enhanced by the prolonging of the microwave reaction time. Such results were thought due to the effect of several factors working together. Firstly, by prolonging the reaction time, the specific surface areas of the prepared  $\text{TiO}_2$  increased slightly as shown in Table 1. Secondly, prolonged reaction time could decrease the amount of adsorbed ammonium groups on the surface of the photocatalysts as discussed before (Fig. 3(A)). Thirdly, although it could not be observed from the XRD patterns, usually a longer reaction time can lead to a better crystallinity of the particles, and this is also considered to be an influencing factor.

Another interesting phenomenon observed is that the generated amount of carbon dioxide was less than double of the decomposed amount of acetaldehyde. According to the process of the oxidative photodegradation of acetaldehyde reported by

Table 1

Specific surface areas of the obtained  $\text{TiO}_2$  powders.

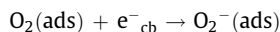
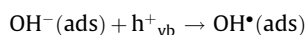
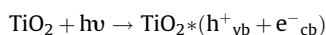
Reaction time (min)	10	30	90
S.S.A. ( $\text{m}^2/\text{g}$ )	200	219	227



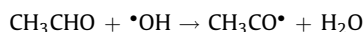
**Fig. 3.** (A) FT-IR spectra of the  $\text{TiO}_2$  powder prepared by the microwave assisted hydrothermal method at  $190^\circ\text{C}$  for (a) 10 min, (b) 90 min, and (c) calcining the sample (b) at  $400^\circ\text{C}$  for 1 h in air. (B) FT-IR spectra of  $\text{TiO}_2$  prepared at  $190^\circ\text{C}$  for 90 min by (a) the microwave assisted and (b) conventional hydrothermal method.

Fujishima et al. [20] the photodecomposition of acetaldehyde could be described in the following steps:

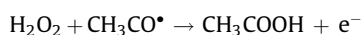
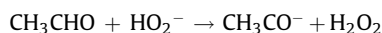
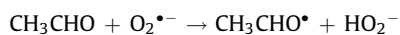
- (1) Photocatalysis



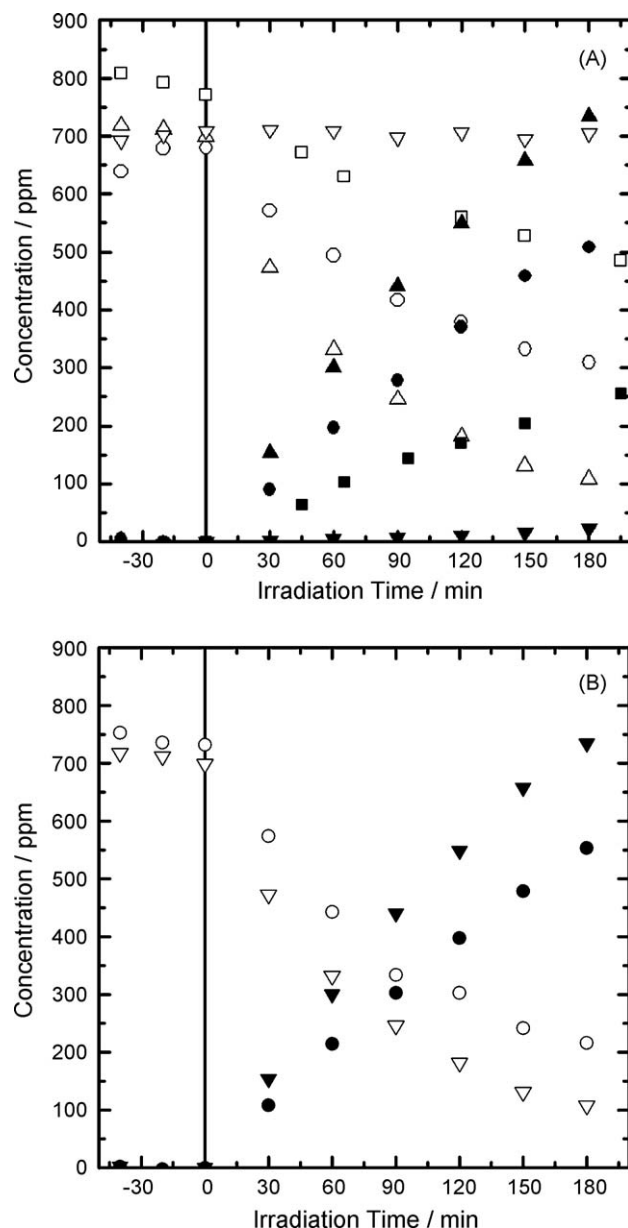
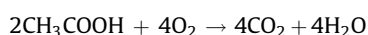
- (2a) Oxidation using hydroxyl radicals:  $\text{OH}^*$



- (2b) Oxidation using superoxide radical:  $\text{O}_2^-$



- (3) Further oxidation under strong illumination



**Fig. 4.** (A) Photocatalytic activities in decomposing acetaldehyde, (a)  $\nabla$ ,  $\blacktriangledown$  blank (irradiation without photocatalyst), and by the  $\text{TiO}_2$  powders prepared by the microwave assisted hydrothermal reactions at  $190^\circ\text{C}$  for (b)  $\square$ ,  $\blacksquare$  10 min, (c)  $\circ$ ,  $\bullet$  30 min, and (d)  $\triangle$ ,  $\blacktriangle$  90 min. (B) Photocatalytic activities in decomposing acetaldehyde by the  $\text{TiO}_2$  prepared at  $190^\circ\text{C}$  for 90 min by (a)  $\nabla$ ,  $\blacktriangledown$  the microwave assisted and (b)  $\circ$ ,  $\bullet$  conventional hydrothermal method. Circle mark refers to the concentration of acetaldehyde, and solid mark refers to that of carbon dioxide.

During the photocatalytic reaction, acetaldehyde is first oxidized to acetic acid. During this stage, no carbon dioxide is generated. Next, the generated acetic acid is further oxidized to carbon dioxide. The obtained results were in good agreement with the suggested reaction profiles that the generation of  $\text{CO}_2$  lagged behind the decomposition of  $\text{CH}_3\text{CHO}$ .

The photocatalytic activities of the  $\text{TiO}_2$  samples obtained from conventional hydrothermal treatment and microwave assisted hydrothermal reaction at  $190^\circ\text{C}$  for 90 min are comparatively shown in Fig. 4(B). It is clear that the sample prepared by the microwave-assisted hydrothermal reaction showed higher photocatalytic activity, probably due to the higher crystallinity and higher anatase content.



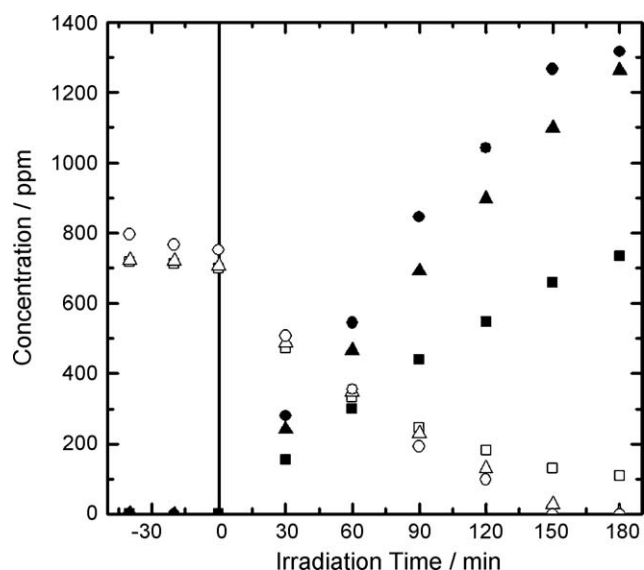


Fig. 5. Photocatalytic activities in decomposing acetaldehyde by the  $\text{TiO}_2$  powders prepared at  $190^\circ\text{C}$  for 90 min (a)  $\square$  before and (b)  $\triangle$  after calcination, and the activity of (c)  $\circ$  AEROXIDE<sup>®</sup>  $\text{TiO}_2$  P 25. Circle mark refers to the concentration of acetaldehyde, and solid mark refers to that of carbon dioxide.

Comparing the activities of  $\text{TiO}_2$ , before and after calcination, it is obvious that calcination at  $400^\circ\text{C}$  for 1 h could enhance the activity, especially the generation rate of carbon dioxide, as shown in Fig. 5. The decomposition rates of acetaldehyde by  $\text{TiO}_2$ , before and after calcination, were almost the same for the first 90 min. On the other hand, even during that period, the generating rate of carbon dioxide by  $\text{TiO}_2$  after calcination was higher than that before. With the reaction time, the decomposition rate of acetaldehyde by  $\text{TiO}_2$  before calcination decreased drastically. This was thought to be due to the poisoning of photocatalysts by the adsorption of intermediate products such as acetic acid. On the other hand, in the case of calcined  $\text{TiO}_2$ , since the generation rate of carbon dioxide was higher, less intermediate products would be left on the surface of the photocatalyst; therefore, the poisoning of the activity could be prevented or delayed. The promotion of photocatalytic activity by the calcination was thought to be due to the better crystallinity. During the heat treatment, the lattice defects, which are usually considered to function as the recombination center of photo-induced electrons and holes, decreased. In addition, on the surface of the photocatalyst, less hydroxyl and ammonium groups existed, which was confirmed by the FT-IR spectra as shown in Fig. 3(A).

To compare the photocatalytic activity of the prepared  $\text{TiO}_2$  with that of the commercial one, the results are also plotted in Fig. 5. It is observed that the prepared  $\text{TiO}_2$  showed equally high photocatalytic activity with that of AEROXIDE<sup>®</sup>  $\text{TiO}_2$  P 25. After photocatalytic reaction for 3 h, about 700 ppm of acetaldehyde was completely decomposed, and the yield of  $\text{CO}_2$  was 87.7% and 89.3% for AEROXIDE<sup>®</sup>  $\text{TiO}_2$  P 25 and our prepared  $\text{TiO}_2$ , respectively. The AEROXIDE<sup>®</sup>  $\text{TiO}_2$  P 25 is widely used as a reference sample in the study of photocatalysis due to its outstanding high activity. It is known that AEROXIDE<sup>®</sup>  $\text{TiO}_2$  P 25 is produced via a high-temperature gas phase reaction using

$\text{TiCl}_4$ , which consumes a huge amount of energy and is in need of corrosion protection.

In this study, a commodity  $\text{K}_2\text{Ti}_4\text{O}_9$  is used as the raw material to prepare  $\text{TiO}_2$  photocatalysts, and compared with other ordinary Ti sources, such as titanium chloride or titanium alkoxides,  $\text{K}_2\text{Ti}_4\text{O}_9$  has the advantage that it is easy to handle. Furthermore, due to the high heating efficiency of microwave, the energy consumption during synthesis is also very low, and nanoparticles with large specific surface areas could be synthesized in a short reaction time without adding any organic species. In other words, this study can offer a novel, environmentally friendly process to prepare high-activity  $\text{TiO}_2$  photocatalyst, which can be widely utilized in environmental purification.

#### 4. Conclusions

Starting from a mature commodity,  $\text{K}_2\text{Ti}_4\text{O}_9$ , well-crystallized  $\text{TiO}_2$  with small crystallite size and high specific surface area was successfully synthesized. The product showed high photocatalytic activity in decomposing acetaldehyde equal to that of the commercial  $\text{TiO}_2$  (AEROXIDE<sup>®</sup>  $\text{TiO}_2$  P 25). Besides new raw material used in this study, a high energy-efficiency synthesis method, microwave-assisted hydrothermal treatment could reduce the energy and time consumption. In addition, no organic solvents or species were employed throughout the synthesis, which greatly simplified the procedures of waste treatment, and reduced the effect of pollution on the environment. In conclusion, a novel and environmentally friendly process to prepare high-activity  $\text{TiO}_2$  photocatalyst was realized in this study.

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